

# Removal of Chromium (VI) Ions by Adsorption Using Riverbed Sand from Tamilnadu – A Kinetic Study

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## Abstract

Various methods adopted for removal of heavy metals include chemical precipitation, membrane separation, ion exchange and adsorption. In case of adsorption, the generally used adsorbents are expensive. This has prompted the use of riverbed sand as adsorbents in order to develop cheaper alternatives. Effect of various experimental parameters such as initial concentration of Cr (VI) ions, adsorbent dosage, contact time, pH of solution and agitation speed were studied. The equilibrium data were analyzed by Freundlich, Langmuir, Tempkin and Dubinin- Radushkevich isotherms. The kinetics of chromium (VI) ions was studied which showed that the adsorption followed pseudo second order reaction. Studies revealed that intraparticle diffusion played important role in the mechanism of Cr (VI) adsorption.

## Keywords:

Riverbed sand, adsorption, equilibrium, kinetics, intraparticle diffusion and chromium.

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## INTRODUCTION:

Heavy metal pollution of wastewater is a common environmental hazard, since the toxic metal ions dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health. The main sources of heavy metal pollution include such as mining, petroleum, textile, milling and surface finishing industries which discharge a variety of toxic metals into the environment [1]. With a rapid increase in global industrial activities, pollution derived from the uncontrolled escape of heavy metals such as copper nickel chromium and zinc has become serious. These heavy metals have harmful effect on human physiology and other biological systems when they exceed the tolerance levels [2]. Among these heavy metals, pollution by chromium is of major concern. The main source of discharge of chromium into the environment is through the effluents coming from various industries such as paints, pigments, dyes, mordant, rubber, plastic, ceramic, textile, leather, tannery, welding processes, smelter works, chrome plating, steel and alloy plants [3,4]. Chromium occurs in aqueous systems in trivalent and hexavalent forms. But the latter

form is of particular concern due to its greater toxicity. When chromium enters the gastric system, epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract and lungs carcinoma are noticed. The discharge limit of chromium from industries is less than 1 mg/L. Chromium is hazardous to health when its limit in potable water exceeds 0.5 mg/L [5].

Conventional methods for removing dissolved heavy metal ions include chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment and evaporative recovery. However, these high technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal [6].

Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Most of the

low cost sorbents have the limitation of low sportive capacity and thereby for the same degree of treatment, which poses disposal problems. Therefore, there is need to explore low cost adsorbent having high contaminant sorption capacity [7]. Consequently numerous low cost alternatives have been studied including Beech sawdust [8], eucalyptus bark [9], green algae [10], seaweeds [11], coir pitch [12], peanut husks carbon [13], Zeolite tuff [14], activated carbon fabric cloth [15], bagasse fly ash [16], activated slag [17], river bed sand [18, 19] etc. New economical, easily available and highly effective adsorbents are still needed. Riverbed sand has the potential to sequester heavy metal ions from solutions. Abundant availability, high sorption capacity, cost-effectiveness, high cation exchange capacity and renewability are the important factors making these materials as economical alternatives for water treatment and waste remediation.

In the present study, experiments were carried out to remove Cr (VI) by adsorption technique using riverbed sand as an adsorbent. Influences of contact time, pH of Cr (VI) solution, effect of agitation speed, effect of adsorbent dose and initial metal ion

concentration are studied under stirred condition. Three different kinetic models for the adsorption of heavy metals are presented. The equilibrium data are tested with Langmuir, Freundlich, Tempkin and D-R isotherm models. This fundamental study will be helpful for further application in designing a batch adsorber for the treatment of heavy metal ion containing effluent coming out from industries.

## EXPERIMENTAL METHODS

All the reagents used for the current investigation were AR grade from Merck Ltd., India.

### Adsorbent collection and preparation

The riverbed sand was collected from Suruliriver named as Suruli Theertham, Theni District, Tamilnadu, India. The soil samples were initially sun dried for 7 days followed by drying in hot air oven at  $383 \pm 1$  K for 2 days. The dried soil was crushed and sieved to give a fraction of 150 mesh screen and then stored in sterile, closed glass bottles till further investigation [18].

### Adsorbate preparation

Stock solution (100 mg/L) of Cr (VI) was prepared by dissolving  $K_2Cr_2O_7$  in double distilled water. The solution was further diluted to the required concentration before use. Before mixing the adsorbent, the pH of each Cr (VI) solution was adjusted to

the required value by 0.1 M NaOH or 0.1 M HCl solution.

### Adsorbent characterization

Adsorbent characterization was performed by means of spectroscopic and quantitative analysis. The results are represented in Table 1.

**Table 1: Physicochemical characteristics of riverbed sand**

S.No	Parameter	Riverbed sand
1	pH	6.9
2	pH <sub>zpc</sub>	2.5
3	Conductivity	0.02dsm <sup>-1</sup>
4	Specific surface area	76.75 cm <sup>2</sup> g <sup>-1</sup>
5	Pore volume	2.494x10 <sup>-3</sup> cm <sup>3</sup> /g
6	Cation exchange capacity	13.1 meq g <sup>-1</sup>
7	Organic carbon	0.27 %
8	SiO <sub>2</sub>	20.66 %
9	Al <sub>2</sub> O <sub>3</sub>	09.76 %
10	Fe <sub>2</sub> O <sub>3</sub>	06.52%
11	CaO	03.05%
12	MgO	00.59%
13	MnO	00.14%
14	Na <sub>2</sub> O	03.33%
15	K <sub>2</sub> O	03.06%

16	P <sub>2</sub> O <sub>5</sub>	00.02%
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## Batch adsorption studies

The batch tests were carried out in glass-stoppered, Erlenmeyer flasks with 200 mL of working volume, with a concentration of 10 mg/L. A weighed amount (0.2 g) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 500 rpm for 90 minute in a magnetic stirrer at 303 K. The influence of pH (2.0–8.0), initial Cr (VI) concentration (10, 20, 30, 40, 50, 60, 70, 90, 100 mg/L), contact time (15, 30, 45, 60, 75, 90 min), adsorbent dose (0.05, 0.075, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4 g) and agitation speed (100, 200, 300, 400, 500, 600, 700, 800 rpm) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual chromium concentration in the solution. The residual amount of chromium in each flask was investigated using UV-VIS spectrophotometer. The amount of Cr (VI) adsorbed in mg/g at time  $t$  was computed by using the following equation:

$$\text{Removal of Chromium (VI) ions by adsorption using riverbed sand from Tamilnadu – A kinetic study:}$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

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(1)

Where  $C_0$  and  $C_t$  are the Cr (VI) concentrations in mg/ L initially and at given time  $t$ , respectively.  $V$  is the volume of the Cr (VI) solutions in ml and  $m$  is the weight of riverbed sand in mg. The amount of Cr (VI) ions adsorbed in milligram per gram was determined by using the following mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where  $q_e$  is the amount of Cr (VI) ion adsorbed onto per unit weight of the adsorbent in mg/g,  $C_0$  is the initial concentration of metal ion in mg/L,  $C_e$  is the equilibrium metal ion concentration in mg/L,  $V$  is the volume of adsorbate in ml and  $m$  is the weight of the adsorbent in mg. The percentage of removal of chromium ions was calculated from the following equation:

$$R (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3)$$

The effect of initial concentration of Cr (VI), contact time, initial pH, adsorbent dosage and agitation speed was investigated by varying any one of the parameters and keeping other parameters constant.

### Adsorption isotherms

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherms were used to describe the equilibrium characteristics of adsorption.

### Freundlich isotherm

This isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent [19]. The linear form of Freundlich equation is expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where  $K_F$  and  $n$  are Freundlich isotherm constants related to adsorption

capacity and adsorption intensity, respectively and  $C_e$  is the equilibrium concentration (mg/L) [20]. The linear plot between  $\log q_e$  versus  $\log C_e$  gives a slope which is equal to the value of  $1/n$  and intercept if  $\log K_F$ . The magnitude of  $1/n < 1$  indicates the favorability of process of adsorption.

### Langmuir isotherm

The Langmuir adsorption isotherm has been successfully used to explain the adsorption of Cr (VI) from aqueous solutions [21]. The linearized Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (5)$$

The Langmuir constants ( $q_m$  and  $K_L$ ) can be calculated from the plot of  $C_e/q_e$  versus  $C_e$ . Where  $q_m$  is a constant and reflects a complete monolayer ( $\text{mg g}^{-1}$ ) and  $K_L$  is adsorption equilibrium constant ( $\text{L mg}^{-1}$ ) that is related to the apparent energy of sorption. The essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor or equilibrium parameter  $R_L$ , which is defined by the following equation [22]

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (6)$$

where  $C_0$  (mg/L) is the initial concentration of adsorbate, and  $K_L$  (L/mg) is Langmuir constant. The value of  $R_L$  indicates the shape of the isotherm which is unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ).

### The Temkin isotherm model

Temkin isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage [23]. The linear form of the Temkin isotherm is represented as:

$$q_e = B \ln A + B \ln C_e \quad (7)$$

Where  $C_e$  is the equilibrium concentration of the adsorbate in mg/L,  $q_e$  is the amount of adsorbate adsorbed at equilibrium (mg/g),  $RT/b_T = B$  where  $T$  is the temperature (K) and  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $A$  and  $b_T$  are constants. A plot of  $q_e$  versus  $\ln C_e$  enables the determination of constants  $A$  and  $B$ . The constant  $B$  is related to the heat of

adsorption and  $A$  is the equilibrium binding constant (L/min) corresponding to the maximum binding energy.

### The Dubinin-Radushkevich isotherm model

The Dubinin-Radushkevich model [24] was chosen to estimate the heterogeneity of the surface energies. The linear form of D-R isotherm equation is represented as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (9)$$

Where  $q_m$  is the theoretical saturation capacity (mol/g),  $\beta$  is a constant related to the mean free energy of adsorption per mole of the adsorbate ( $\text{mol}^2/\text{J}^2$ ) and  $\varepsilon$  is the polanyi potential,  $C_e$  is the equilibrium concentration of adsorbate in solution (mol/L),  $R$  ( $\text{J mol}^{-1} \text{ K}^{-1}$ ) is the gas constant and  $T$  (K) is the absolute temperature. The D-R constants  $q_m$  and  $\beta$  were calculated from the linear plots of  $\ln q_e$  versus  $\varepsilon^2$ . The constant  $\beta$  gives an idea about the mean free energy  $E$  (kJ/mol) of adsorption per molecule of the adsorbate when it is

transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship [25]:

$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

If the magnitude of  $E$  is between 8 and 16  $\text{kJ mol}^{-1}$ , the sorption process is supposed to proceed via chemisorption, while for values of  $E < 8 \text{ kJ mol}^{-1}$ , the sorption process is of physical nature [25].

### Adsorption kinetics

In order to investigate the adsorption of Cr (VI) on the surface of riverbed, different kinetic models are used to examine the controlling mechanism of adsorption process. The proposed kinetic models are based on literature for sorption processes and adsorption capacity of adsorbent. In this study pseudo-second-order kinetic model and intra-particle-diffusion are investigated to find the best fitted model for the experimental data.

### The pseudo first-order equation

The pseudo first-order equation [26] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (11)$$

where:  $q_e$  and  $q_t$  are the adsorption capacity at equilibrium and at time  $t$ , respectively ( $\text{mg/g}$ ),  $k_1$  is the rate constant of pseudo first-order adsorption ( $1/\text{min}$ ).

After integration and applying boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (12)$$

The values of  $\log(q_e - q_t)$  were linearly correlated with  $t$ . The plot of  $\log(q_e - q_t)$  vs.  $t$  should give a linear relationship from which  $k_1$  and  $q_e$  can be determined from the slope and intercept of the plot, respectively.

### The pseudo second-order equation

The pseudo second-order adsorption kinetic rate equation is expressed as [27]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (13)$$

where:  $k_2$  is the rate constant of pseudo second-order adsorption ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ).

For the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the integrated form of Eq. (13) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k t \quad (14)$$

which is the integrated rate law for a pseudo second-order reaction. Equation (14) can be rearranged to obtain Eq. (15), which has a linear form:

$$\left( \frac{t}{q_t} \right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \quad (15)$$

if the initial adsorption rate,  $h$  ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$ ) is:

$$h = k_2 q_e^2 \quad (16)$$

then Eqs. (15) and (16) become:

$$\left( \frac{t}{q_t} \right) = \frac{1}{h} + \frac{1}{q_e} (t) \quad (17)$$

The plot of  $(t/q_t)$  and  $t$  of Eq. (5) should give a linear relationship from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively.

### The intraparticle diffusion model

For a solid – liquid adsorption process, the solute transfer is usually

characterized by external mass transfer, or intraparticle diffusion, or both. The intraparticle diffusion model is expressed by Weber and Morris [28] was used to identify the mechanism involved in adsorption process:

$$q_t = K_{id} t^{0.5} + A \quad (18)$$

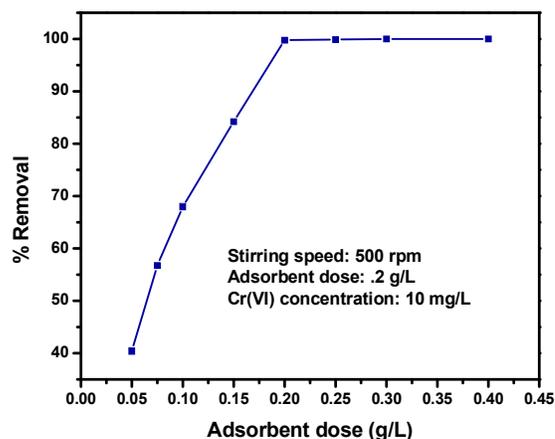
where  $K_{id}$  ( $\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$ ) is intraparticle diffusion rate constant and  $A$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is a constant that gives an identification of thickness of boundary layer. Greater the value of  $A$  greater is the effect of boundary layer on adsorption process. If the rate limiting step be the intra-particle diffusion, the plot of  $q_t$  against the square root of time should be a straight line pass through the origin. The deviation from linearity indicates the rate limiting step should be boundary layer (film) diffusion controlled.

## Results and discussion

### Effect of adsorbent dosage

For economic removal of Cr (VI) from waste water, it is necessary to find the optimum amount of adsorbent for efficient removal. The relationship between the

percentage removal of Cr (VI) and amount of riverbed sand is shown in figure. 1 it can be seen that as the amount of the riverbed sand increases from 0.025 to 0.4 g/L the percentage of adsorption increase from 0.025 to 0.2 g/L. Further increases of adsorbent amount beyond 0.2 g/L do not affect the adsorption significantly this observation can be explained in terms of availability of active sites on the adsorbent surface. The increasing trend in adsorption percentage as adsorbent dosage increases might be attributed to the increases of surface area and presence of additional availability sites [30]. The adsorbent dosage was inversely proportional to the adsorption capacity of riverbed sand this is because increase in adsorbent dosage might have led to the overlapping of surface area due to the restricted area made available and therefore led to reduction of effective surface area which plays an important role in metal uptake [31, 32].

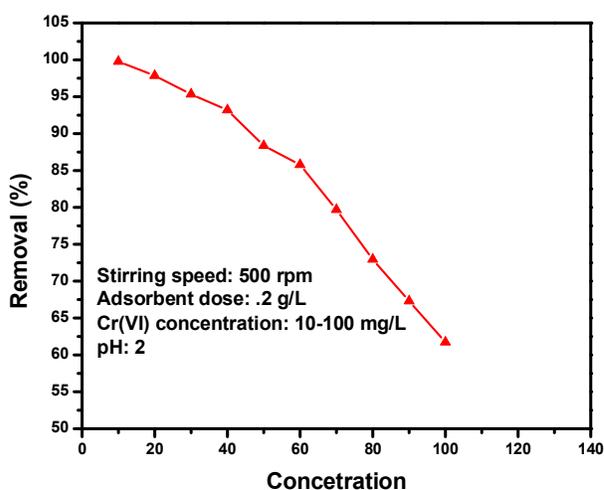


**Figure 1 Effect of adsorbent dosage on Cr (VI) removal**

#### Effect of initial Cr (VI) concentration

The initial concentration of Cr (VI) provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases. Figure 2 shows that when the initial Cr (VI) ion concentration increased from 10 – 100 mg/L, Cr (VI) adsorption removal decreased from 99.99% to 61.45% and the uptake capacity of riverbed sand increased. The decrease in removal percent was due to the saturation of the sorption sites on adsorbents. In addition, the increasing in uptake capacity of riverbed sand with increasing of Cr (VI) ion concentration is due to higher availability of Cr (VI) ions in

the solution, for the adsorption and this can be attributed to an increase in driving force of the concentration gradient with increase in concentration of Cr (VI) in solution. Apparently, the initial concentration of chromium plays an important role and affects the adsorption capacity of Cr (VI) on adsorbent. It is clear from the figure that in initial stages the removal/adsorption percentage is higher in lower ranges of concentration.



**Figure 2 Effect of initial concentration on Cr (VI) removal**

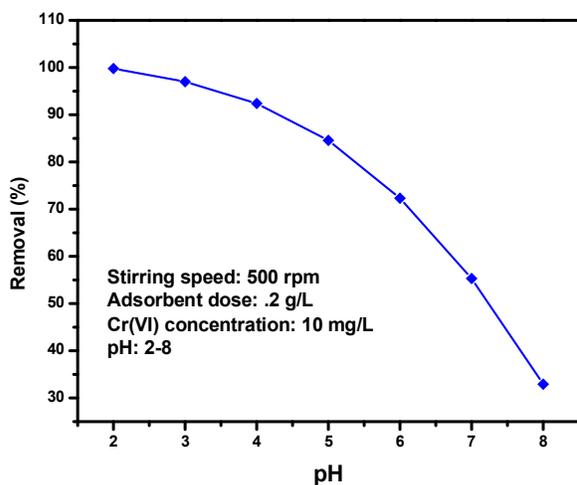
### Effect of pH

The wastewater from industries usually has a wide range of pH values. Thus pH of the system plays an important role in

the wastewater treatment. The value of pH affects both aqueous chemistry and surface binding sites of the adsorbents. The effect of solution pH on the removal of chromium during adsorption process shown in figure. Removal of Cr (VI) was high in acidic and low in alkaline medium. Removal decreased from 99.99% to 30.95% by increasing pH of the solution from 2 to 8 at 10 mg/L initial concentration, 30 °C, 100 µm particle size, 500 rpm agitation speed and 0.2 g/L adsorbent dose. The removal efficiency was highly pH dependent, the percentage uptake of Cr (VI) decreased gradually with an increase in pH. Figure 3 shows the effect of pH on Cr (VI) removal efficiency.

The dependence of metal removal on the pH can be explained from the perspective of surface chemistry in aqueous phase, the surface of riverbed sand containing metal oxides are gradually covered with hydroxyl groups that vary in form at different pH. The surface charge is neutral at zero point of charge pHzpc, which is 2.5 for riverbed sand. Below the pHzpc, the adsorbent surface is positively charged and anion adsorption occurred by simple electrostatic attraction. Above the pHzpc, the adsorbent surface is negatively charge

and cation adsorption occurred with an increase in pH. The uptake of Cr(VI) ions decreased, which is apparently due to the higher concentration of  $\text{OH}^-$  ions present in the mixture that compete with Cr (VI) species ( $\text{CrO}_4^{2-}$ ) for adsorption sites. On the other hand, as adsorption surface is negatively charged ( $\text{pH} < \text{pH}_{\text{zpc}}$ ) increasing electrostatic repulsion between the negatively charged Cr (VI) species and negatively charged riverbed sand would also result in a release of adsorbed  $\text{HCrO}_4^{4-}$  and  $\text{CrO}_4^{2-}$ .



**Figure 3 Effect of pH on Cr (VI) removal**

### Effect of agitation speed

The effect of agitation speed rate on Cr (VI) adsorption is shown in Figure 4 and

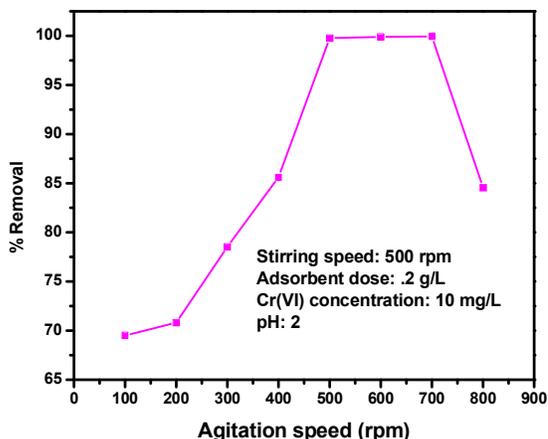
it appears agitation speed has pronounced effect on the amount of Cr (VI) adsorbed. As the agitation speed increased from 100 to 500 rpm, the percentage removal increased from 69.5 % to 99.99 %. However beyond 500 rpm, the adsorption percentage remained constant and the agitation speed of 500 rpm was selected in subsequent analysis. The increase in adsorption capacity at a higher agitation speed could be explained in terms of the reduction of boundary layer thickness around the adsorbent particles [33].

Therefore, with increasing agitation speed the concentrations of Cr (VI) ions near the adsorbent surface would be increased. A higher agitation speed also encourages a better mass transfer of Cr (VI) ions from bulk solution to the surface of the adsorbent and shortened the adsorption equilibrium.

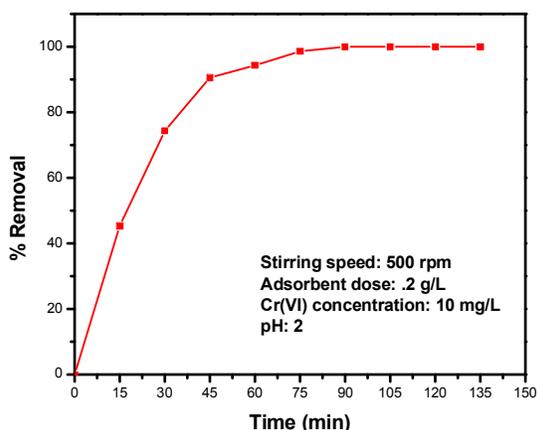
### Effect of contact time

The absorbed amounts of metal ions at different time intervals were determined and plotted against time were shown in figure 5. It is clear from the figure that adsorbed amount of Cr (VI) constantly increases with increasing time and then acquires a constant value. It happens because the rate of metal ions binding with

microspheres is more at initial stage which gradually decreases and remains constant after an optimum adsorption.



**Figure 4 Effect of agitation speed on Cr (VI) removal**



**Figure 5 Effect of contact time on Cr (VI) removal**

### Adsorption isotherm

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Adsorption isotherm also usually describes the equilibrium relationship between adsorbent and adsorbate. The correlation coefficient ( $r^2$ ) value for the equilibrium curve is the most significant parameter to optimize the design of an adsorption system to remove dyes from effluents. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption.

The linear plot of Langmuir isotherm for Cr (VI) adsorption and the calculated parameters along with regression coefficients are shown in Fig.6 and Table 2, respectively. Maximum adsorption capacity,  $q_m$ , for complete monolayer coverage are found 1.6181 mg/g for 0.2 g/l.  $R^2$  values approaching to one (0.998), clearly suggest that Langmuir isotherm follows a good relation of Cr (VI) adsorption with riverbed

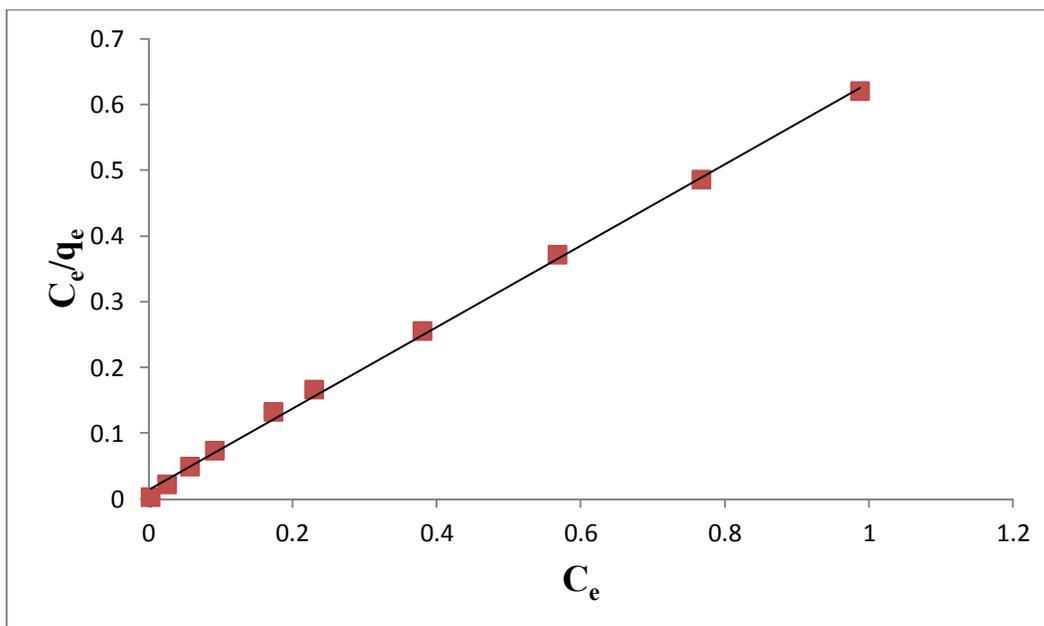
sand. ' $K_L$ ' is the adsorption constant related to the affinity of binding sites (l/g) and lower value of ' $K_L$ ' (l/g for three doses) indicate that the particles radius of riverbed sand were small toward adsorption [35]. The value of  $R_L$  (0.977) revealed that Cr (VI) adsorption on riverbed sand is favorable as the values lies between 0 and 1.

### erm constants for Cr (VI) adsorption onto riverbed sand

**Table 2: The Isotherm constants for Cr (VI) adsorption onto riverbed sand**

Table	Isotherm models	parameters	
2: The Isoth	Langmuir isotherm	$R^2$	0.998
		$K_L$	0.023
		$q_m$ (mg/g)	1.618
		$R_L$	0.977
	Freundlich isotherm	$R^2$	0.941
	$K_F$	1.218	
	N	12.19	
Tempkin isotherm		$R^2$	0.913
		$B_T$	1618.9
		A	0.105
D-R isotherm		$R^2$	0.696
		$\beta$	0.002
		$q_m$ (mg/g)	0.35
		E (kJ/mol)	15.822

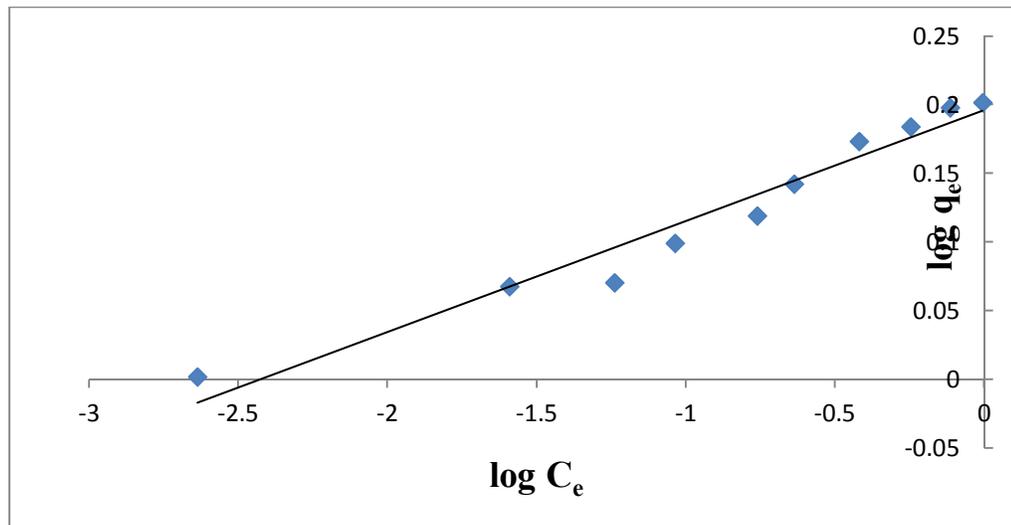




**Figure 6. Linear plot of Langmuir isotherm for adsorption of Cr VI) on riverbed sand**

The linear plot of Freundlich equation for Cr (VI) adsorption and the calculated parameters are shown in Figure 7 and Table 2, respectively.  $K_F$  is a Freundlich constant that shows adsorption capacity on heterogeneous sites with non-uniform distribution of energy level and  $n$  shows the intensity between adsorbate and adsorbent. Compared with the correlation

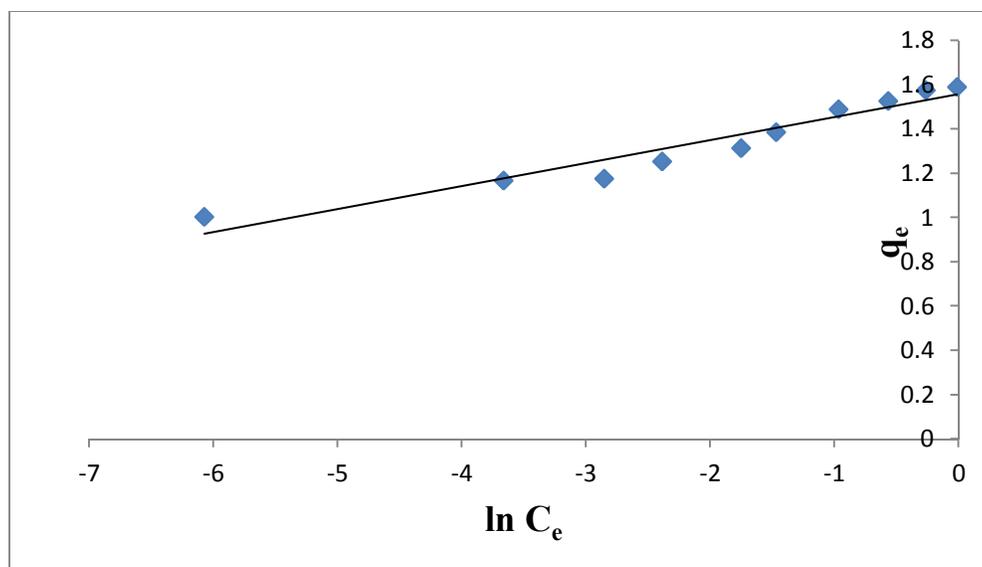
coefficient value of linear plot of Langmuir isotherm, that of Freundlich model was found to less satisfactory. In this study the  $n$  values are greater than unity indicating chemisorption. Isotherms with  $n > 1$  are classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and it is indicative of chemisorption.



**Figure 7. Linear plot of Freundlich isotherm for adsorption of Cr VI) on riverbed sand**

Figure 8 and Table 2 shows Temkin isotherm and calculated constant of adsorption ( $b_T$ ). Linear plots for Temkin adsorption isotherm, which consider chemisorptions of an adsorbate onto

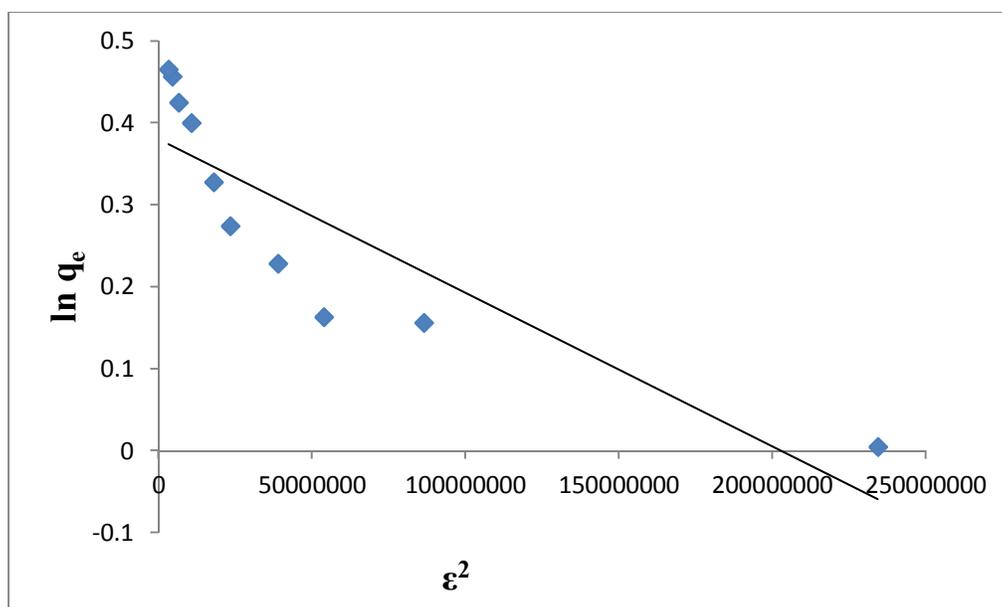
adsorbent, fit quite with correlation coefficients  $\geq 0.913$ . This further supports the findings that the adsorption of Cr (VI) onto riverbed sand is a chemisorptions process.



**Figure 8. Linear plot of Temkin isotherm for adsorption of Cr VI) on riverbed sand**

The slope and intercept of plots of  $\ln q_e$  versus  $\varepsilon^2$  were used to calculate the D-R isotherm parameters  $\beta$  and  $q_m$  show in table 3 and figure 9. The  $q_m$  values are not consistent with the  $q_m$  values previously determined for Langmuir isotherm. The

magnitude of the correlation coefficients for D-R isotherm model is lower when compared to other three isotherm models. This suggests that the Cr (VI) adsorption onto riverbed sand is not a physical process.



**Figure 9. Linear plot of D-R isotherm for adsorption of Cr (VI) on riverbed sand**

### Kinetic studies

Values of correlation coefficients for these equations determined by non-linear regression for all kinetic models, pseudo-first and pseudo-second order and intra-particle equation for adsorption of Cr (VI) onto riverbed sand are listed in Table 2 and

figures 10, 11, 12. The correlation coefficient ( $r^2$ ) for the linear plots of pseudo-second order reaction plots is better than the pseudo first-order plots. This shows that the pseudo-second order kinetic model explains the sorption in better way. The pseudo-

second order model is based on the assumption that the rate determining step may be a chemical sorption involving valance forces through sharing or exchanging electrons between sorbent and sorbate [34]. If the intraparticle diffusion involved in the adsorption process, then the plot of the square root of time versus the uptake would result in a linear relationship and the intraparticle diffusion would be controlling step if this line is passed through the origin. When the plots donot pass through the origin, this indicative of some degree of boundary layer control and this

further shows that the intraparticle diffusion is not the only rate controlling step, but also other process may control the rate of adsorption [35]. The values of  $k_{id}$  were calculated from the slope of such plots and the  $r^2$  values led to the conclusion that the intraparticle diffusion process is the rate-limiting step. Higher values of  $k_{id}$  illustrate an enhancement in the rate of adsorption, whereas larger  $k_{id}$  values illustrate a better adsorption mechanism, which is related to an improved bonding between Cr(VI) ions and the adsorbent particles.

**Table 2: Different kinetic model parameters**

Models	Parameters	
	$q_{e, \text{exp}}$ (mg/g)	1.004
Pseudo-first order model	$R^2$	0.182
	$k_1$ ( $\text{min}^{-1}$ )	0.0207
	$q_{e, \text{cal}}$ (mg/g)	1.3458
Pseudo-second order model	$R^2$	0.961
	$h$ (mg/g min)	0.1034
	$k_2$ (g/mg min)	0.0834
	$q_{e, \text{cal}}$ (mg/g)	1.135

Intra-particle diffusion model	$R^2$	0.956
	$K_{id}$ (mg/g min <sup>-0.5</sup> )	8.543
	A (mg/g)	2.452

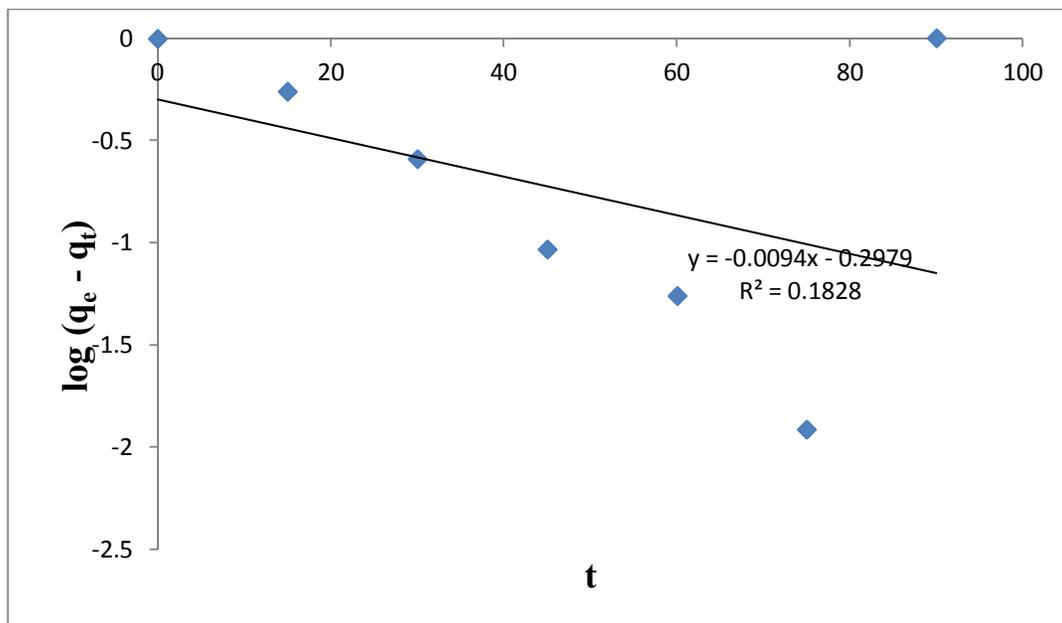
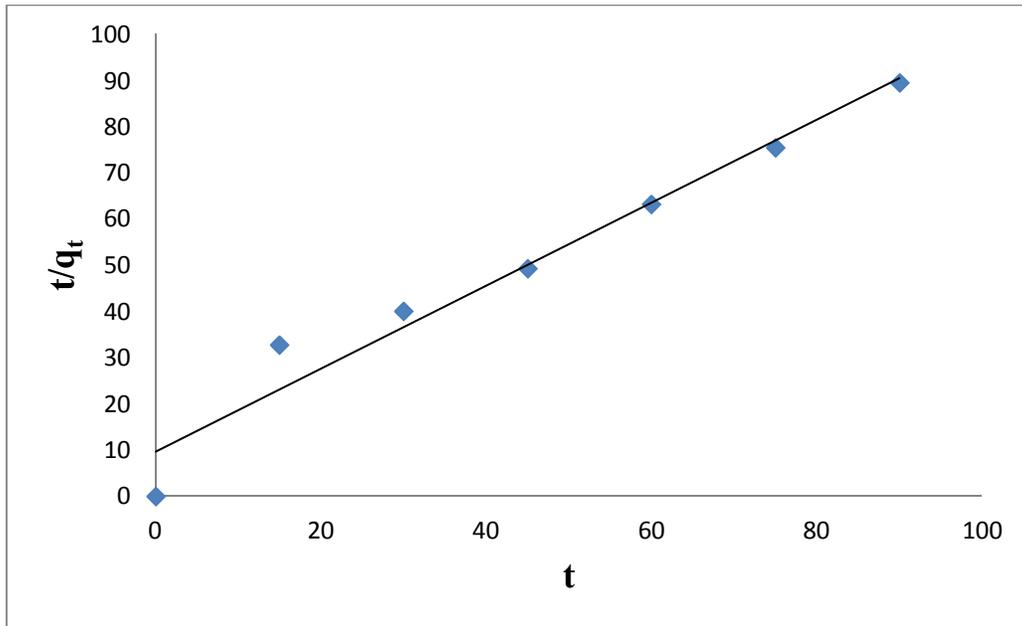
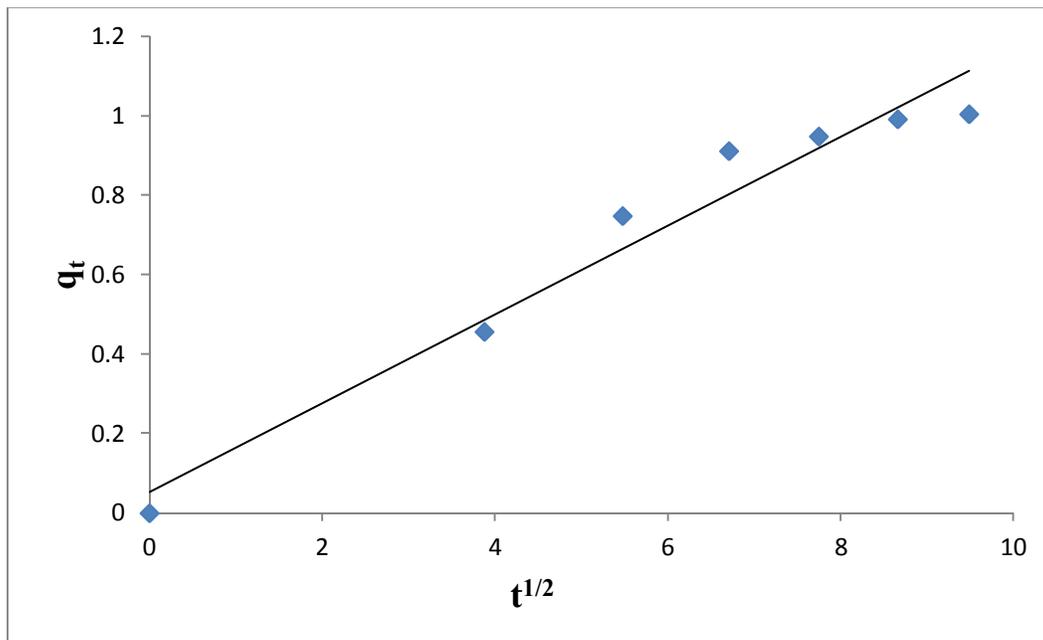


Figure 10 Linear plot of Pseudo-first order model



**Figure 11 linear plot of pseudo-second order model**



**Figure 12 plot of intra-particle diffusion model**

## Conclusion

The removal of Cr (VI) from aqueous solutions using riverbed sand was studied under batch adsorption mode under different conditions. The results of this investigation show that riverbed sand has a suitable adsorption capacity for the removal of Cr (VI) from aqueous solutions. The experimental results well fitted with

Langmuir, Freundlich and Tempkin isotherm models. The data indicate that the adsorption kinetics follow the pseudo-second order kinetics with intra-particle diffusion as one of the rate determining step. The present study concludes that the riverbed sand could be employed as low cost and eco-friendly adsorbent for the removal of Cr (VI) ions from wastewater.

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